

GROWTH AND CHARACTERISATION OF PURE AND THIOUREA DOPED ROCHELLE SALT CRYSTALS BY SLOW EVAPORATION METHOD

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ABSTRACT:

Transparent single crystals of Pure and Thiourea doped Rochelle salt (Sodium Potassium Tartrate) was successfully grown by slow evaporation method at room temperature. Studies of the grown crystals were carried out by Powder X-ray diffraction analysis to find out the crystalline nature. The different modes of vibration and the functional groups present in pure and thiourea doped SPT were identified by FTIR spectra. The wide optical transparency in entire visible region was shown by UV-Vis-Spectral analysis. Vicker's microhardness test was carried out to test the mechanical stability and the hardness parameters are determined. The TG/DTA and DSC studies confirm the thermal stability and crystallinity of the grown crystals.

KEYWORD:

Rochelle salt, Powder XRD, Single Crystals, Thermal analysis, Hardness.

1. INTRODUCTION

In the past previous decades, there has been a growing interest on crystals growth processes, particularly in the view of increasing demand of materials for technological application [1,2]. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals [3]. The reasons for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The main advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research.

Growing of crystals owing to a number of technological applications in the field of micro-electronics and opto-electronics, a great deal of interest has been shown in studying the properties of various materials[4-6]. Semi-organic crystals which have the combined properties of both inorganic and organic crystals such as wide application for device fabrication [7]. The Rochelle salt being optically active [8] strongly piezoelectric molecule exhibiting a non-centrosymmetrical structure can be easily obtained when tartaric acid reacts with some bases [9] has attracted much research interest because it exhibits ferroelectric and paraelectric phase properties from low to high temperatures [10]. The Rochelle salt is of particular interest as it

exhibits a ferroelectric phase between 255 and 297 K, where the structure is monoclinic with a space group of $P2_1$, above the temperature of 297 K the compound is paraelectric and exhibits an orthorhombic phase in space group $P2_12_12$ [11]. Investigation of the dielectric properties of the Rochelle salt shows anomalies at low temperature. The tartarate molecules lie in three planes, bonded to sodium and potassium atoms directly through a medium of water molecules [12]. Earlier reports infer that RS (Rochelle Salt) has two sub lattices, in high temperature neither of the sub lattices are polarized hence the crystal is not ferroelectric [13,14]. Crystals of different orientations with different morphology are grown by conventional solution growth technique but from an application point of view, specific orientation with good quality is needed.

Crystallization from solution is an important process and the driving force for crystallization is the degree of supersaturation which has been commonly expressed as the difference in concentration between the supersaturated and saturated solutions [15].

2. EXPERIMENTAL

2.1 SLOW EVAPORATION METHOD

This method is similar to slow cooling method in view of apparatus requirement. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth condition involves temperature stabilization to about $+0.003^\circ\text{C}$ and rates of evaporation of a few mm^3/hour . The evaporation techniques of crystal growth have the advantage that the crystals grown at a fixed temperature. This method is the only way, which can be used for materials of very small temperature coefficient of solubility.

2.2 MATERIALS AND METHODS

Analytical grade (AR) samples of Rochelle salt and Thiourea along with triple distilled water were used for the growth of single crystals by slow evaporation methods at room temperature.

Solubility of SPT was maintained in the temperature range 30°C to 35°C and the growth solution was prepared according to the solubility data. The dopant thiourea in various concentrations (0.0002M, 0.0005M, 0.0007M and 0.0009M) was added to the parent crystal SPT. The solution was stirred at 30°C and left undisturbed with protection from dust for slow evaporation.

3. RESULT AND DISCUSSION

3.1. FOURIER TRANSFORM INFRARED ANALYSIS (FTIR)

The O-H stretching vibration gives a broad band at about 3000 cm^{-1} . The fine structure is due to hydrogen bonding. The fine structure is due to hydrogen bonding. In the higher wavelength region, the peak at 3779 cm^{-1} is assigned to O-H stretching vibration. The region 3511 cm^{-1} and 3107 cm^{-1} with strong intensity represents N-H stretching mode. The broad envelope positioned in between 3503 cm^{-1} and 2773 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH_2 group. The peak at 3080 cm^{-1} with medium intensity refers C-H asymmetric stretching. Combinational overtones extend to the bands from $2359 - 2364\text{ cm}^{-1}$. The peak at

1638 cm^{-1} indicating the C=O stretching mode of vibration. The NH_2 bending vibrations occur at 1618, 1619 and 729 cm^{-1} .

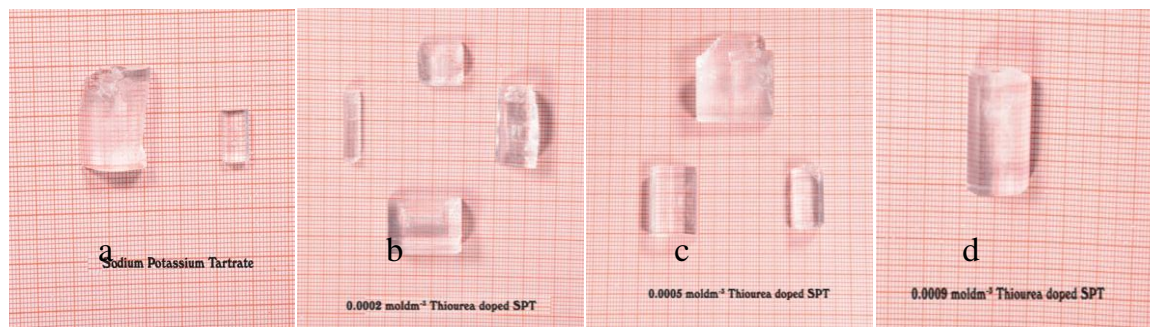


Fig.1 Crystals of Pure Rochelle salt (a) and Thiourea doped (b, c and d) Rochelle salt grown from solution.

Asymmetric bending of NH_3^+ and C=N stretching present at the peak 1606 cm^{-1} . The peak at 1498 cm^{-1} is due to NH_2 bending vibration. CH_2 deformation vibrations are identified by the sharp band at 1470 cm^{-1} . The peaks at 1415 – 1413 cm^{-1} corresponds to the C=S stretching. The C-C stretching mode of vibration. The spectra show absorption bands in the region of 1168 cm^{-1} and 1068 cm^{-1} which are due to in-plane C-H bending vibration. The band 1128 cm^{-1} signifies the N-H symmetric bending. C-C-N stretching vibration obtained at 1083-1078 cm^{-1} . The bands at 867 cm^{-1} and 805 cm^{-1} revealed that C-N deformation mode. The ring deformation occurs the peak at 822 cm^{-1} . C=O deformation is identified by the band at 696 cm^{-1} . C-H out-of plane bending peaks obtained at 667 cm^{-1} and 668 cm^{-1} . The bands 630-633 cm^{-1} represents C-C deformation. The absorption bands in the region of 486-491 cm^{-1} which are due to N-C-N stretching vibration. The assignments confirm the presence of various functional groups present in the material. The weak absorption at 1608 cm^{-1} indicates the presence of NH_3^+ and C=N stretching vibration. The absorption around 1619 cm^{-1} in NH_2 bending and this band would be shifted into lower wavelength region 1618 cm^{-1} compared with our investigations were well compared with earlier reports [16-25] The FTIR spectrum of pure and thiourea doped SPT shown figure 2 and 3

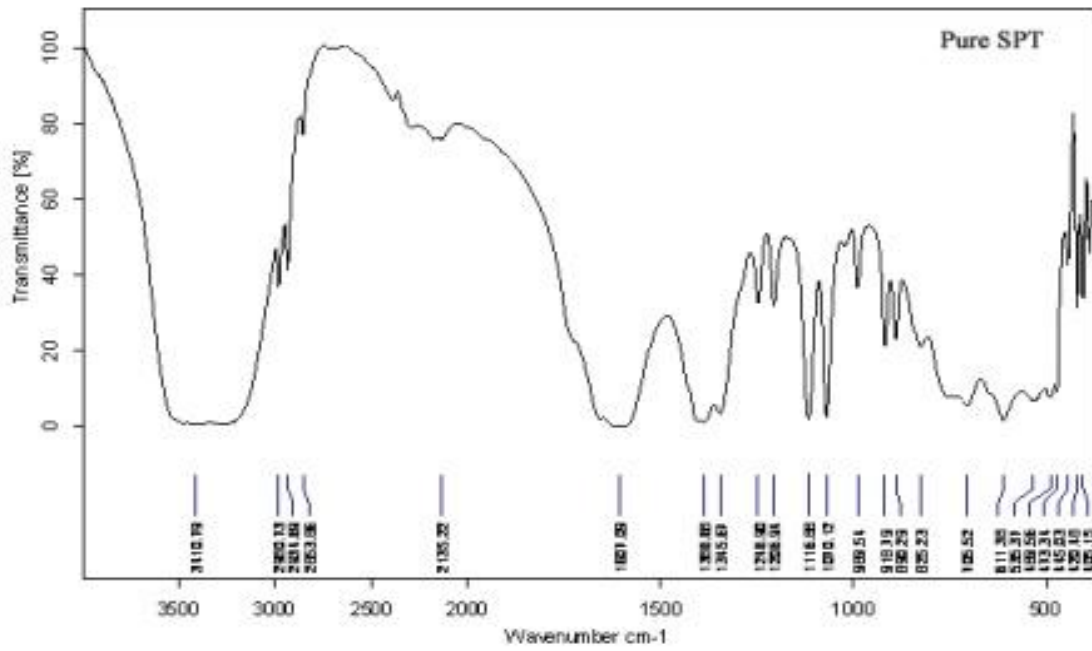


Fig.2 FTIR Spectrum of pure Rochelle salt crystal

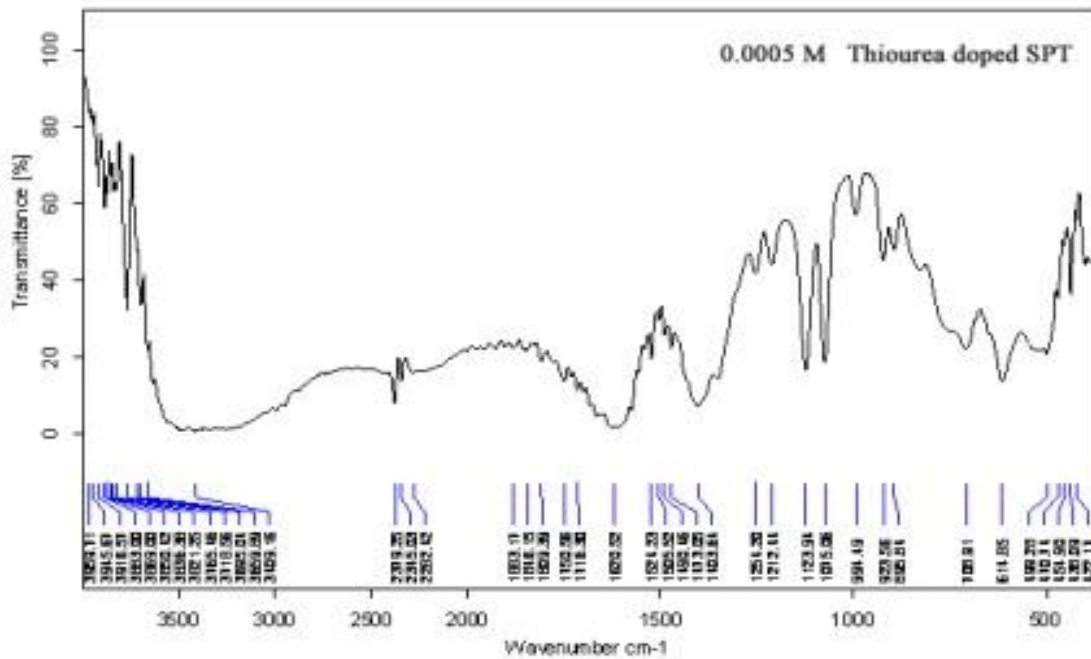


Fig.3 FTIR Spectrum of Thiourea doped Rochelle salt crystal

3.2 Powder X-ray diffraction analysis:

Powder X-ray diffraction was performed to confirm the quality of the crystals and to identify the cell dimensions using Bruker A X3D8 PERT-PRO, advance model powder diffractometer with CuK α radiations ($\lambda = 1.5405984 \text{ \AA}$). It is also used to confirm the physical phase of the crystals.

The powder diffraction experiments were conducted using crystallites directly instead of powder, the peak intensity indeed reflect the proportion of every plane and orientations of crystal growth. According to present calculations {100} planes have the largest area for X-ray irradiations, which gives rise to the strongest peak intensity of {200} peak. Other diffraction peaks (i.e. Intensities) mainly depend on the plane area and probability to be irradiated, the high Miller index planes of small crystallities have more probability irradiated by X-ray big ones, the smaller crystallites and the strongest peak intensity, which can be detected in figure 4. Pure and thiourea doped SPT interplanar space and intensity were compared in Table-1.

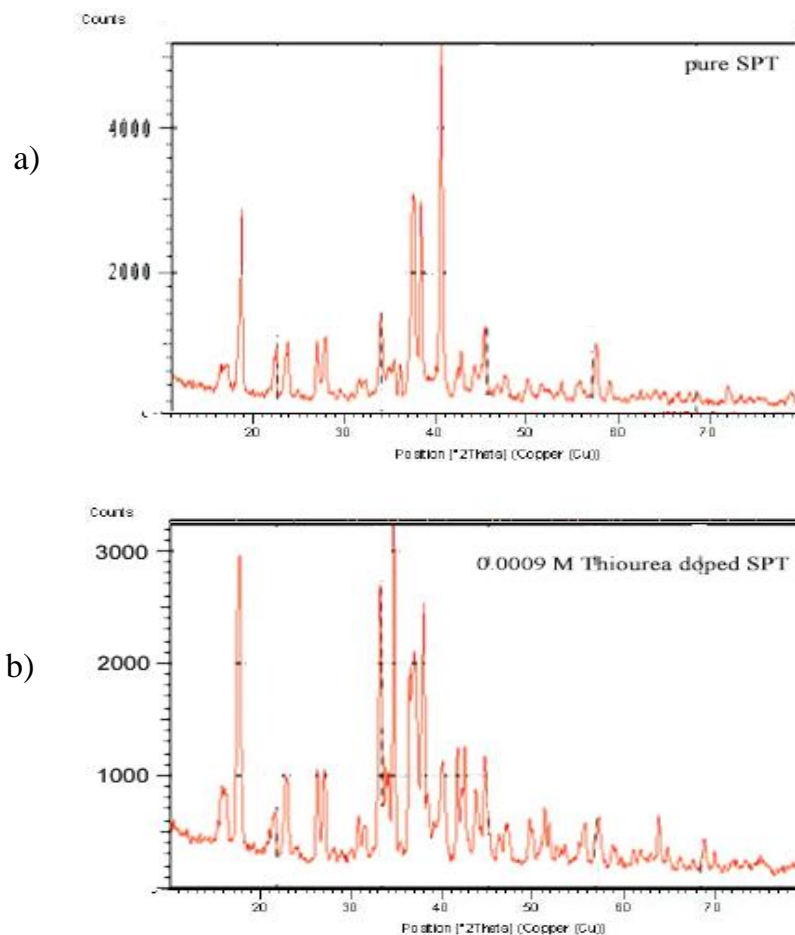


Fig.4 Powder XRD Pattern of Pure (a) and Thiourea (b) doped Rochelle salt crystals

Table.1 Indexed XRD data for pure SPT and Thiourea doped SPT

S.No.	Pure SPT			Thiourea doped SPT		
	2Theta (deg)	d (Å)	Intensity	2Theta (deg)	d (Å)	Intensity
1.	14.7000	6.0212	120	14.5000	6.1038	68
2.	15.3000	5.7864	151	14.9000	5.9408	208
3.	16.6202	5.3296	873	15.3000	5.7864	190
4.	19.8663	4.4655	248	16.5270	5.3595	1033
5.	21.0012	4.2267	290	19.3000	4.5952	51
6.	23.8825	3.7229	289	19.8234	4.4751	146
7.	24.5997	3.6159	349	20.9688	4.2331	299
8.	27.8000	3.2065	88	21.9222	4.0511	41
9.	28.4000	3.1401	88	23.9189	3.7173	334
10.	29.9028	2.9856	455	24.5365	3.62513	317
11.	30.6000	2.9162	150	27.7000	3.2178	111
12.	31.2000	2.8644	198	28.3215	3.1486	111
13.	31.7603	2.8151	151	29.8102	2.9947	960
14.	32.4000	2.7610	82	30.5000	2.9285	303
15.	32.9913	2.7128	1191	31.0957	2.8737	1183
16.	33.7353	2.6547	1025	31.6843	2.8217	50
17.	35.6760	2.5146	1839	32.5000	2.7527	555
18.	37.1000	2.4213	102	33.0000	2.7121	705
19.	37.6000	2.3902	234	33.8135	2.6487	799
20.	38.8000	2.3190	165	34.3000	2.6123	218
21.	39.7291	2.2669	336	34.9000	2.5687	114
22.	40.9990	2.1996	62	35.6662	2.5153	346
23.	41.7513	2.1616	127	37.0519	2.4243	350
24.	43.8933	2.0610	110	37.6233	2.3888	390
25.	45.2052	2.0042	76	38.1000	2.3600	53

3.3 Microhardness study

Hardness test is useful to find the mechanical hardness of the crystal and to estimate the threshold mechanical stress. Vickers hardness measurement of pure and thiourea doped SPT crystals were noted by applying loads of 25g, 50g and 100g for a indentation time of 7 sec, for each trial. Repeated trials were performed to ascertain the correctness of the observed results. The Vickers microhardness number (H_V) was calculated using the relation.

$$H_V = \frac{1.8544 p}{d^2} \quad (\text{Kg} / \text{mm}^2)$$

where p is the indenter load in Kg and d is the diagonal length of the impression in mm. From the figure 5 it is seen that the hardness value of the thiourea doped SPT crystal is comparatively higher than the pure SPT crystals. This is due to the incorporation of thiourea in to the pure SPT crystals.

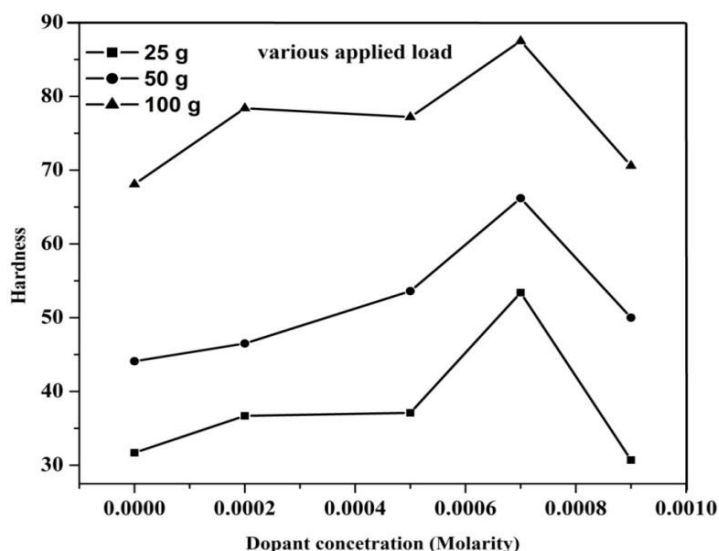


Fig.5 comparative vickers hardness of Pure and Thiourea doped Rochelle salt crystals

3.6 Thermal Studies

The TG/DTA thermogram for powdered potassium sodium tartrate tetrahydrate (Rochelle salt) was recorded in nitrogen atmosphere with a heating rate of 15°C/min using STA 409PC instrument. The TGA thermogram is as shown in figure.6. It reveals that there were three stages of decomposition. The TGA trace appears nearly straight up to its melting point showing the thermal stability of the grown crystal. The melting and decomposition occur simultaneously. The first stage of decomposition in

DTA is due to the elimination of water molecule from the crystal lattice. The second stage of decomposition is due to the evolution of CO_2 molecules from the crystal lattice due to breaking of the carboxyl group. After decomposition the material has a residue of 46.39% which is shown in TG thermograms. Further, a sharp melting point of pure SPT at 74.6°C is observed with shown a good degree of crystallinity of the grown ingot. The onset of decomposition of SPT is observed at 122.1°C and ends at 135.3°C . Adding of Thiourea dopant into the SPT, incorporation of thiourea into the pure SPT crystal and make the crystal hard. From the figure 6, the Thiourea doped SPT crystal showed a sharp melting point of pure SPT at 73.7°C is observed with shown a good degree of crystalline of the grown ingot. The onset of decomposition of SPT is observed at 124.3°C and ends at 140.7°C stepwise decomposition implies the phase transition occurring in the compound

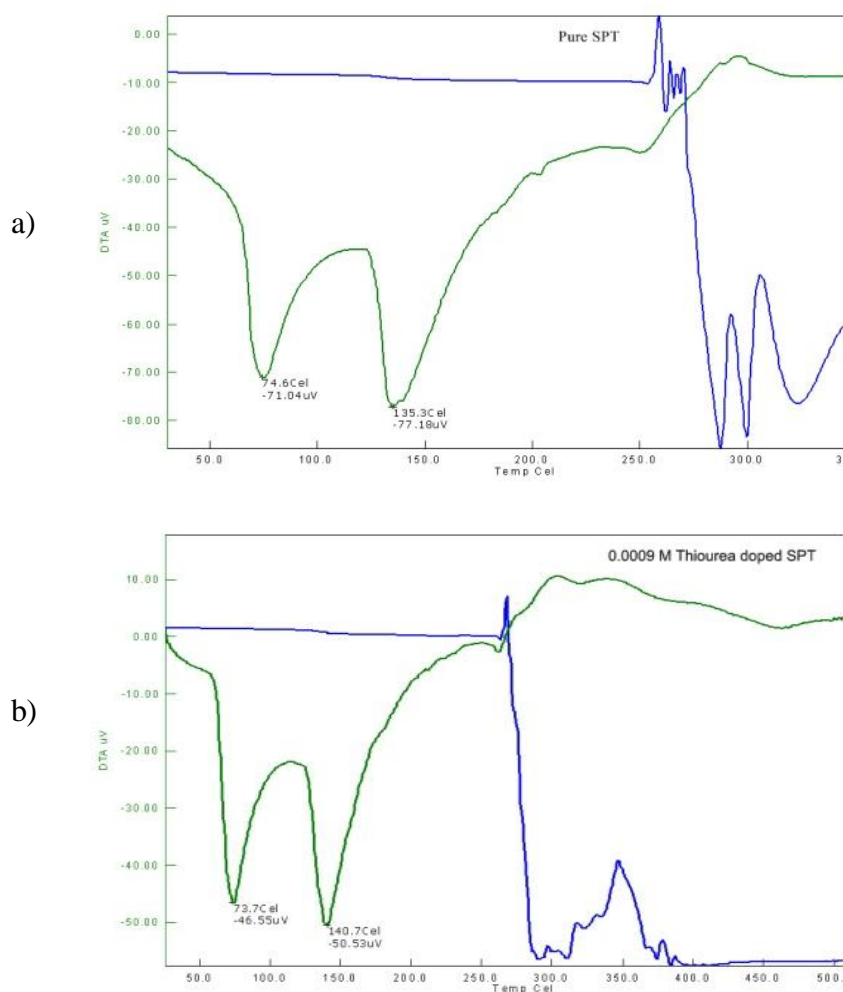


Fig. 6 TG/DTA Spectrum of Pure Rochelle salt (a) and Thiourea doped Rochelle salt crystals

4.CONCLUSIONS

From the present investigation it is understood that the thiourea doping distorts the normal crystal lattice significantly. Single crystals of Pure SPT and Thiourea doped SPT crystals were grown by slow evaporation technique at room temperature. The presence of thiourea in SPT lattice was confirmed qualitatively by both powder and FTIR analysis. Thermal studies revealed the hardness, stability, melting point and decomposition temperature of the pure and doped SPT crystals. Thiourea doped SPT crystals showed higher hardness and decomposition temperature due to the incorporation thiourea SPT domain. The powder X-ray diffraction analysis confirmed the crystal system of Pure SPT and Thiourea doped SPT crystals. Appearance of sharp well defined peaks in XRD confirms the crystallinity of the sample. The microhardness of Thiourea doped SPT crystals showed higher hardness than the Pure SPT crystals This is due to the incorporation of Thiourea into the Pure SPT lattice. The value of 0.0007M Thiourea doped SPT crystal showed higher hardness. Thermal study gave the idea about the stability, decomposition temperature and melting point of both pure and Thiourea doped SPT crystals. The stability of the Thiourea doped SPT is greater than Pure SPT as expected to be higher H-bonding due to the Thiourea.

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